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Global occurrence of tellurium-rich ferromanganese crusts and a model for the enrichment of tellurium

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Abstract—Hydrogenetic ferromanganese oxyhydroxide crusts (Fe-Mn crusts) precipitate out of cold ambient ocean water onto hard-rock surfaces (seamounts, plateaus, ridges) at water depths of about 400 to 4000 m throughout the ocean basins. The slow-growing (mm/Ma) Fe-Mn crusts concentrate most elements above their mean concentration in the Earth's crust. Tellurium is enriched more than any other element (up to about 50,000 times) relative to its Earth's crustal mean of about 1 ppb, compared with 250 times for the next most enriched element.

We analyzed the Te contents for a suite of 105 bulk hydrogenetic crusts and 140 individual crust layers from the global ocean. For comparison, we analyzed 10 hydrothermal stratabound Mn-oxide samples collected from a variety of tectonic environments in the Pacific. In the Fe-Mn crust samples, Te varies from 3 to 205 ppm, with mean contents for Pacific and Atlantic samples of about 50 ppm and a mean of 39 ppm for Indian crust samples. Hydrothermal Mn samples have Te contents that range from 0.06 to 1 ppm. Continental margin Fe-Mn crusts have lower Te contents than open-ocean crusts, which is the result of dilution by detrital phases and differences in growth rates of the hydrogenetic phases.

Correlation coefficient matrices show that for hydrothermal deposits, Te has positive correlations with elements characteristic of detrital minerals. In contrast, Te in open-ocean Fe-Mn crusts usually correlates with elements characteristic of the MnO₂, carbonate fluorapatite, and residual biogenic phases. In continental margin crusts, Te also correlates with FeOOH associated elements. In addition, Te is negatively correlated with water depth of occurrence and positively correlated with crust thickness. Q-mode factor analyses support these relationships. However, sequential leaching results show that most of the Te is associated with FeOOH in Fe-Mn crusts and ≤10% is leached with the MnO₂.

Thermodynamic calculations indicate that Te occurs predominantly as H₅TeO₆[−] in ocean water. The speciation of Te in ocean water and charge balance considerations indicate that Te should be scavenged by FeOOH, which is in agreement with our leaching results. The thermodynamically more stable Te(IV) is less abundant by factors of 2 to 3.5 than Te(VI) in ocean water. This can be explained by preferential (not exclusive) scavenging of Te(IV) by FeOOH at the Fe-Mn crust surface and by Fe-Mn colloids in the water column. We propose a model in which the extreme enrichment of Te in Fe-Mn crusts is likely the result of an oxidation reaction on the surface of FeOOH. A similar oxidation process has been confirmed for Co, Ce, and Tl at the surface of MnO₂ in crusts, but has not been suggested previously to occur in association with FeOOH in Fe-Mn crusts. Mass-balance considerations indicate that ocean floor Fe-Mn deposits are the major sink for Te in the oceans. The concentration and redox chemistry of Te in the global ocean are likely controlled by scavenging on Fe-Mn colloids in the water column and Fe-Mn deposits on the ocean floor, as is also the case for Ce. Copyright © 2003 Elsevier Science Ltd

1. INTRODUCTION

It has been suggested that Te is unique in the universe in that its cosmic abundance is as great or greater than that of any other element with an atomic number higher than 40 (Cohen, 1984; <http://www.webelements.com>), yet it is one of the least abundant elements in the Earth's crust and in ocean water. In addition, Te is abundant in plants and primary consumers, such as humans (700 ppb; Table 1), even though it occurs in extremely low concentrations in soils (Cohen, 1984; Emsley, 1999). These conclusions are based on sparse data and need to be further investigated, but our data set on Te in ferromanganese oxyhydroxide crusts (Fe-Mn crusts) is representative of

these deposits in the oceans and shows that Te holds an exclusive place in terms of its enrichment relative to the Earth's crust.

Fe-Mn crusts precipitate out of cold ambient ocean water (hydrogenetic) onto hard-rock surfaces at water depths of ~400 to 4000 m throughout the ocean basins. Fe-Mn crusts precipitate at the incredibly slow rates of 1 to 6 mm/Ma, which combined with their extreme specific surface area (325 m²g^{−1}), promotes the enrichment of most elements in the periodic table above their mean concentration in the Earth's crust (continental plus oceanic crust; Hein et al., 2000). The only exceptions are the major rock-forming elements and also notably Au and Pd. Fe-Mn crusts have traditionally been called Co-rich crusts because Co is strongly enriched and is the incorporated metal with the greatest economic potential. However, on geologic grounds, Fe-Mn crusts could properly be called Te-rich crusts.

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Table 1. Content of Te in various materials.

Material	Content (ppb)	Measured	Source
Fe-Mn crusts	6,000 – 52,000	Range of means	This study, Lakin et al. (1963)
Seafloor massive sulfides	<1 – 10,000	Range ^a	Butler and Nesbitt (1999)
Abyssal Fe-Mn nodules	5,000	Mean	Baturin (1988)
C1 chondrites	2,320	Mean	Anders and Grevesse (1989)
Pelagic clay	1,000	Mean	Baturin (1988)
Human body (70 kg)	700	Mean	Emsley (1999)
OIB, Loihi glass	5 – 29	Range	Yi et al. (2000)
The silicate earth	12	Mean	McDonough and Sun (1995)
Volcanic arcs, Mariana	2.3 – 6.2	Range	Yi et al. (2000)
MORB	0.8 – 7.5	Range	Yi et al. (2000)
Earth's crust	0.36 – 10	Range of estimates	From three compilations ^b
River water (Ming R.)	2.8×10^{-3}	Mean	Jingru and Qing (1983)
Seawater	5.10×10^{-5} to 1.66×10^{-4} (0.4–1.3 pM)	Range	Lee and Edmond (1985)
	$2.4\text{--}8.7 \times 10^{-4}$ (1.9–6.8 pM)	Range	Andreae (1984)
	6×10^{-4} ($3\text{--}9 \times 10^{-4}$)	Mean (and range)	Sugimura and Suzuki (1981)
	4.7 pM (2.4–7.1 pM)		Jingru and Quing (1983)

^a Rarely up to 45,000 ppb.

^b Parker (1967), Levinson (1974), and Govett (1983).

Tellurium is unique among the elements in that it is concentrated in Fe-Mn crusts to a greater degree than any other relative to its concentration in the Earth's crust (Fig. 1). For example, whereas mean contents of the elements heretofore known to be most enriched in Fe-Mn crusts, Mn, Co, Mo, Bi, Tl, and As are enriched 100 to 250 times over their Earth's crustal value, the mean Te content in central Pacific hydroge- netic Fe-Mn crusts is enriched ~55,000 times. However, the distribution of Te in the Earth is poorly known. Estimates of the mean Te content of the Earth's crust range from 0.36 to 10 ppb (Table 1), with 1 to 2 ppb being the most commonly cited estimates of mean content (compilations in Parker, 1967; Levinson, 1974; Govett, 1983). If we use the upper-bound crustal estimate of 10 ppb, then Te concentrations in Fe-Mn crusts would be 5500 times greater than the estimated maximum Earth's crustal value, ~22 times more enriched than the

next most enriched element. This unusually high enrichment is created either by an underestimate in the Earth's crustal Te content, or unique processes that enrich Fe-Mn crusts in Te. The mean Te content of the Earth's crust would have to be ~220 ppb for its enrichment factor to equal that of the next most enriched element in Fe-Mn crusts. Because of these unique characteristics of Te, we describe its global distribution in Fe-Mn crusts and propose a model for its enrichment.

Tellurium, like Te, is not mined as a primary ore anywhere in the world. Rather, Te is produced as a byproduct of Cu and Au mining. The high concentrations of Te in Fe-Mn crusts warrant consideration of crusts as a potential Te ore should the demand for Te increase. This demand may be driven by new applications in solar cell technology that uses high-purity Te (Brown, 2000).

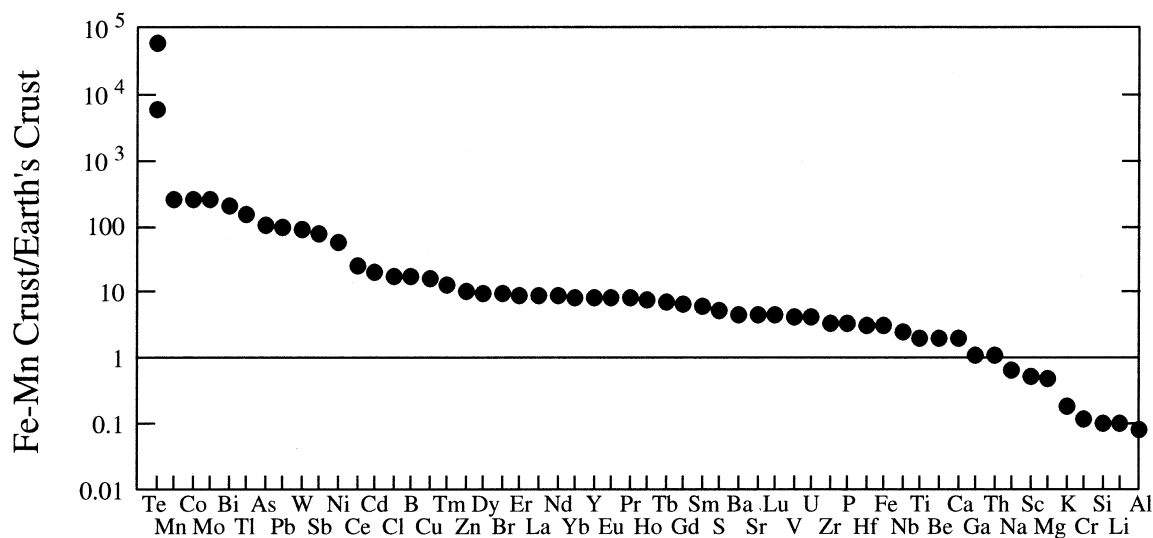


Fig. 1. Enrichment of elements in Fe-Mn crusts relative to mean abundances in the Earth's crust; the two values for Te are based on an Earth's crustal mean of 1 and 10 ppb.

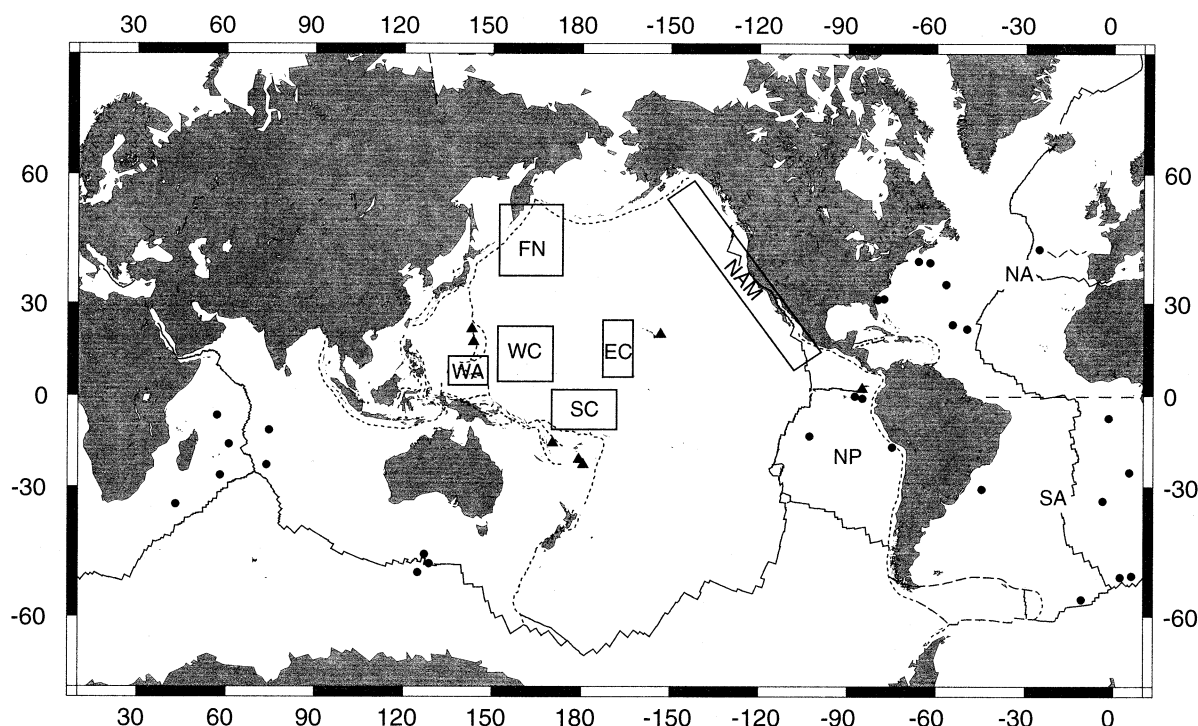


Fig. 2. Distribution of samples used in this study. Letters indicate areas listed in Table 2, and the *n*-values in Table 2 list the number of samples in each area: FN = far north; WA = western arcs; WC = west central; SC = south central; EC = east central; NAM = North American margin; NP = Nazca Plate. Filled circles are locations of hydrogenetic Fe-Mn crusts outside the boxed areas and filled triangles are hydrothermal Mn deposits. The dashed line at the equator divides the North Atlantic (NA) from the South Atlantic (SA).

2. SAMPLES

Fe-Mn crusts are composed of up to eight macroscopic texturally distinct layers and vary in thickness from a patina to 250 mm (Hein et al., 2000). The Fe-Mn crusts analyzed here vary in thickness from ~2 to 180 mm. Fe-Mn crusts are composed of poorly crystalline δ -MnO₂ (vernadite), whereas marine stratabound hydrothermal Mn-oxide deposits (hydrothermal Mn) and abyssal Fe-Mn nodules are composed of various combinations of todorokite, birnessite, and vernadite. Most abyssal nodules form when Mn and Fe oxides accrete around a nucleus at or near the sediment surface by both hydrogenetic (from ocean water) and diagenetic (from pore waters) precipitation. Hydrothermal Mn forms below the sediment-water interface from the mixing of reduced hydrothermal fluids with oxic seawater at relatively low temperatures (<100°C; Hein et al., 1997). The older parts of thick Fe-Mn crusts also contain diagenetic carbonate fluorapatite (CFA; up to 30%) that impregnated and partly replaced the crusts and substrate rocks during two phosphogenic events that took place near the Eocene–Oligocene and Oligocene–Miocene boundaries (Hein et al., 1993). Quartz and feldspar are minor detrital components in most Fe-Mn crusts. X-ray amorphous FeOOH also makes up a significant proportion of Fe-Mn crusts, which crystallized to goethite in ~6% of 640 crusts analyzed by Hein et al. (2000).

Bulk Fe-Mn crust refers to the entire crust thickness, whereas layers refer to texturally distinct layers within individual crusts whose composite sum equals the total crust thickness. For this

study, we analyzed a suite of 76 bulk crusts and 110 individual crust layers from Pacific sites; 19 bulk crusts and 17 crust layers from Atlantic sites; 6 bulk crusts and 7 crust layers from Indian Ocean sites; and 4 bulk crusts and 6 crust layers from sites south of Australia (Fig. 2). In addition, for comparison, we analyzed 10 hydrothermal Mn samples collected from a variety of tectonic environments in the Pacific, including the Mariana, Yap, and Tonga volcanic arcs; Lau basin and North Fiji basin back-arc spreading centers; Hawaii submarine rift zones; Blanco transform fault; and the Galapagos spreading center.

3. METHODS

Tellurium contents were determined by graphite furnace atomic-absorption spectrometry and Mn, Fe, Si, Al, Mg, Ca, K, Ti, P, Ba, Nb, and Zr were determined by X-ray fluorescence spectrometry. Cobalt, Cu, Mo, Ni, Pb, Sr, V, and Zn were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) and Bi, Cd, Ga, Sn, Tl, and rare earth elements by ICP-mass spectrometry (ICP-MS). Arsenic, Cr, Hf, Sb, Se, and W were determined by neutron activation analysis and S by combustion and infrared spectrometry. All chemical data were normalized to 0% hygroscopic water (H₂O⁺) because of the variable but strong hygroscopic nature of Fe-Mn crusts (15 to 30% H₂O⁺; see Hein et al., 2000, for discussion). Details of these techniques can be found in Baedeker (1987).

Five samples were subjected to a sequential-leaching procedure. These samples include a hydrogenetic crust from the central Pacific where the nonphosphatized and phosphatized layers were leached separately, one crust from the Atlantic that does not have a phosphatized layer, and two hydrothermal samples from North Fiji Basin. Sequential leaches were designed to identify elements associations with four phases (detailed methods in Koschinsky and Halbach, 1995;

Table 2. Statistics for Te contents (ppm) in hydrogenetic Fe-Mn crusts and for comparison hydrothermal Mn deposits.^a

Data set	n	Mean	Median	SD	Min.	Max.
All data	245	46	43	33	3	205
All bulk	105	43	40	29	4	176
All layers	140	48	45	36	3	205
Pacific, all data	186	52	46	31	3	191
Bulk	76	46	44	27	4	145
Layers	110	56	47	34	3	191
Far north	19	27	23	14	12	72
North American margin	20	9	9	3	3	18
Nazca plate	17	24	19	10	15	46
East-central	11	46	46	25	10	89
West-central	103	65	56	28	29	191
Bulk	43	61	55	23	32	145
Layers	60	68	59	31	29	191
South-central	10	29	23	17	10	67
Western arcs	6	31	33	12	9	43
Atlantic, all data	36	48	38	45	5	205
Bulk	19	39	31	38	5	176
Layers	17	59	42	52	15	205
North	21	35	35	17	5	67
South	15	67	45	64	10	205
Indian, all data	13	39	25	25	9	74
South of Australia	10	24	19	13	14	56
Hydrothermal	10	~0.3	~0.2	0.3	0.06	1.0

^a n = number of samples; SD = standard deviation; Min = minimum; Max = maximum.

Koschinsky and Hein, 2003): carbonate plus loosely bound exchangeable phases (1 mol/L acetic acid buffered to pH 5); Mn-oxide (0.1 mol/L hydroxylamine at pH 2); Fe-oxyhydroxide (0.2 mol/L oxalate buffered to pH 3.5); and residual fraction (concentrated acids with a final matrix of ~1 mol/L HNO₃). Elements associated with the CFA would be found mostly in the residual leach, but also in the FeOOH leach. The solutions were analyzed by both ICP-AES and ICP-MS.

Statistical analyses were performed on 40 data sets. In addition to analysis of all combined data, analyses were performed on subsets from ocean basins, including the North Atlantic, the South Atlantic, and the various divisions of the Pacific shown in Figure 2 (23 of those data sets are listed in Table 2). In addition, each geographic data set and subset was analyzed using chemical data for bulk crusts and crust layers. The usual Pearson product moment correlation coefficient was used to calculate correlation coefficient matrices (Davis, 1986). A 95% confidence level was used for data sets with a small number of samples and a 99% level for large data sets. Q-mode factor analysis is concerned with the interobject relationships in a data set that are needed to place those objects (elements in our case) into common groups. These groups are called "factors," and on the basis of X-ray diffraction mineralogy and element correlations, we interpret each factor to represent a particular mineral or phase in the Fe-Mn crusts and the elements in that factor to be associated with that mineral or phase. For our Q-mode factor analysis, each percentage was scaled to the percent of the maximum value. Subsequently, values were row normalized and cosine theta coefficients were calculated. Factors were derived from orthogonal rotations of principal component eigenvectors by the Varimax method (Klovan and Imbrie, 1971). Elements with rotated factor scores below |0.12| were not included because random noise makes it difficult to resolve the orientation of the factor to within 10° of an absolute direction in variable space. All communalities, an index of the efficiency of a reduced set of factors to account for the original variance, are ≥0.90.

4. RESULTS

4.1. Composition and Distribution

Observed Te concentrations in Fe-Mn crusts vary from 3 to 205 ppm. Mean contents for Pacific, Atlantic, Indian, and south

of Australia crusts are 52, 48, 39, and 24 ppm, respectively (Table 2). The global mean for bulk Fe-Mn crusts is 43 ppm. Continental margin Fe-Mn crusts have lower Te concentrations than open-ocean crusts. The west-central Pacific and the south Atlantic crusts have the highest mean (65 and 67 ppm) and maximum (191 and 205 ppm) Te contents (Table 2). The lowest mean and minimum Te concentrations occur offshore North America, 9 and 3 ppm, respectively. For comparison, hydrothermal Mn samples have Te concentrations that range from 0.06 to 1.0 ppm.

4.2. Statistical Analyses of Fe-Mn Crust Compositions

Correlation coefficient matrices for hydrothermal deposits show that Te has a positive correlation only with Cu. In contrast, Te in open-ocean hydrogenetic crusts correlates with elements characteristic of the MnO₂, CFA, and residual biogenic phases (Table 3). In detail, the correlations are somewhat different among regions, but the most significant and regionally most consistent Te correlations are with Bi, Co, Mn, and Sr and to a lesser degree, Tl, Pb, Ti, S, Zn, Ca, P, and Nb. In less than 50% of the investigated regions, other notable Te correlations are observed with Sn, Ga, Ni, Cr, Ba, W, and Fe. In crusts from the west-central Pacific and south of Australia, Te has a positive correlation with both Mn and Fe (Table 3), otherwise it has a positive correlation with Mn and a negative correlation with Fe. In all data sets for open-ocean crusts, Te shows a negative correlation, or no correlation, with elements characteristic of the detrital-aluminosilicate phase (e.g., Si, Al, K, and commonly Fe and Cu). Like manganophile elements (elements associated with MnO₂, e.g., Co, Ni) in Fe-Mn crusts, Te is negatively correlated with water depth of occurrence and, like Pt, is positively correlated with crust thickness. That latter relationship is interesting because it indicates that grade increases with tonnage of the potential ore.

Correlations with Te are somewhat different and fewer (at the 95% confidence level) for crusts from continental margins. For example, Te correlates only with Fe (representative of FeOOH) in bulk crusts from off North America (Fig. 2; Table 3) and with Fe, Nb, W, and Zr for crust layers from that same area. This difference in correlations between bulk crust and crust layer data is the result of the greater range of data for individual layers. Other continental margin regions (North Atlantic, far North Pacific, west Pacific arcs; Fig. 2) also show fewer 95% confidence level correlations than are found in data sets for crusts from open-ocean regions. All data sets where Te correlates with Fe have mean Fe/Mn ratios greater than 1 in contrast to data sets for crusts from open-ocean regions.

Q-mode factor analysis delineates two to five factors depending on the data set (Fig. 3). We interpret those factors to represent the MnO₂, FeOOH, CFA, residual biogenic material, and aluminosilicate-detrital minerals, which occur in 100, 40, 48, 33, and 90% of the data sets, respectively. Tellurium occurs in both the FeOOH and MnO₂ factors in the data set for all bulk crusts (Fig. 3). Tellurium occurs in the MnO₂ factor in half of the 40 data sets, in the CFA factor in a third of the data sets, and in only 12% of each of the other three factors. Tellurium is associated statistically with the MnO₂ factor in all 12 of the Atlantic and Indian data sets and also with CFA in four of those data sets (see example in Fig. 3). In the Pacific data sets, Te

Table 3. Correlation coefficient matrices for selected elements for 4 of 40 Fe-Mn crust data sets; the zero point of correlation for A at the 99% confidence level is $|0.252|$; and for B, C, and D at the 95% confidence level are $|0.454|$, $|0.301|$, and $|0.706|$.

	Fe	Mn	Al	P	Te	Co	Ni
A. All bulk crusts data (n = 105)							
Mn	-0.030						
Al	0.496	-0.506					
P	-0.474	0.001	-0.299				
Te	-0.303	0.413	-0.443	0.384			
Co	-0.359	0.495	-0.565	-0.053	0.494		
Ni	-0.509	0.506	-0.498	0.071	0.226	0.642	
Bi	-0.463	0.427	-0.528	0.439	0.614	0.492	0.403
B. Atlantic Ocean bulk crusts (n = 19)							
Mn	0.187						
Al	0.169	-0.442					
P	-0.647	-0.169	-0.323				
Te	-0.065	0.756	-0.488	0.149			
Co	0.241	0.704	-0.556	-0.059	0.846		
Ni	-0.531	0.290	0.000	0.202	0.246	0.171	
Bi	-0.018	0.675	-0.542	-0.005	0.831	0.761	0.041
C. West Central Pacific Ocean bulk crusts (n = 43)							
Mn	0.531						
Al	0.633	0.038					
P	-0.186	-0.227	-0.062				
Te	0.361	0.304	0.143	0.276			
Co	-0.194	0.364	-0.291	-0.492	-0.036		
Ni	-0.278	0.306	-0.360	-0.186	-0.194	0.610	
Bi	0.014	-0.008	-0.220	0.407	0.460	-0.019	0.073
D. North American Margin bulk crusts (n = 8)							
Mn	0.025						
Al	0.344	-0.617					
P	0.646	0.016	-0.152				
Te	0.768	0.298	0.111	0.290			
Co	-0.166	0.800	-0.776	0.307	-0.037		
Ni	-0.638	0.620	-0.477	-0.678	-0.250	0.408	
Bi	0.063	0.650	-0.640	0.473	0.147	0.876	0.060

occurs about an equal number of times in each of the factors depending on region and crust type. Tellurium is associated with the factor for the aluminosilicate-detrital factor only in continental margin data sets, as well as in the hydrothermal Mn data set. The MnO_2 factor includes the elements, in order of decreasing rotated factor scores: Mn, Co, Tl, Ni, Mo, Pb, Te, Bi, V, W, Sr, and S; the CFA factor includes Ca, P, Sr, S, Bi, Te, Zn, and Mo; and the most common FeOOH factor elements include Fe, Ti, Zr, Hf, Ga, S, Sn, and Zn.

4.3. Sequential Leaching

Sequential leaching shows that most (77 to 84%) of the Te is leached with the FeOOH in three Fe-Mn crusts (Table 4; also see Koschinsky and Hein, 2003), and only 8 to 10% is leached with the MnO_2 . The diagenetic phosphatization of the crust apparently shifts some of the Te to the CFA, which would be leached predominantly with the residual phases. Note that significant amounts of Fe are leached with the MnO_2 , which results in part from incomplete separation of phases during the leaching procedure and in part from the Mn mineral being a ferruginous vernadite. Also note that Mn is found virtually solely with the leach for MnO_2 . Q-mode factor analysis of the leach data places Te only in the Fe factor.

In the two hydrothermal Mn samples (Table 4), a greater proportion of Te leaches with the dominant Mn oxide rather than with the minor FeOOH . These two samples have very low

Fe/Mn ratios, 0.06 and 0.005. Much of the Fe (42 and 65%) leaches with the residual aluminosilicate phases, whereas only 2% of the Te is in the residual leach. More than twice as much Te is in the loosely bound phases in the hydrothermal Mn samples compared with the Fe-Mn crust samples.

The discrepancy between the association of Te predominately with the MnO_2 based on statistical analyses and with the FeOOH based on sequential leaching is the result of a number of factors. Iron in Fe-Mn crusts is distributed among all of the phases including the MnO_2 (ferruginous vernadite), aluminosilicate, biogenic, CFA, as well as the discrete FeOOH . Consequently, it is the relative proportions of Fe in all these phases that will determine, in part, its statistical phase associations and the strength of those associations. Correlation coefficients and factor analysis are based on a comparison of variance of the elements in our analyses. Manganese and Te are nearly exclusively enriched in Fe-Mn crusts by hydrogenetic processes, whereas Fe is also derived from detrital and other inputs. Consequently, the Mn and Te variance may be more similar than the Fe and Te variance even if Te is bound to Fe.

5. DISCUSSION

5.1. Global Distribution

Tellurium falls among the group of elements (Pb, Co, Mn, Ce, Eu, and Sm) most enriched in Fe-Mn crusts relative to their

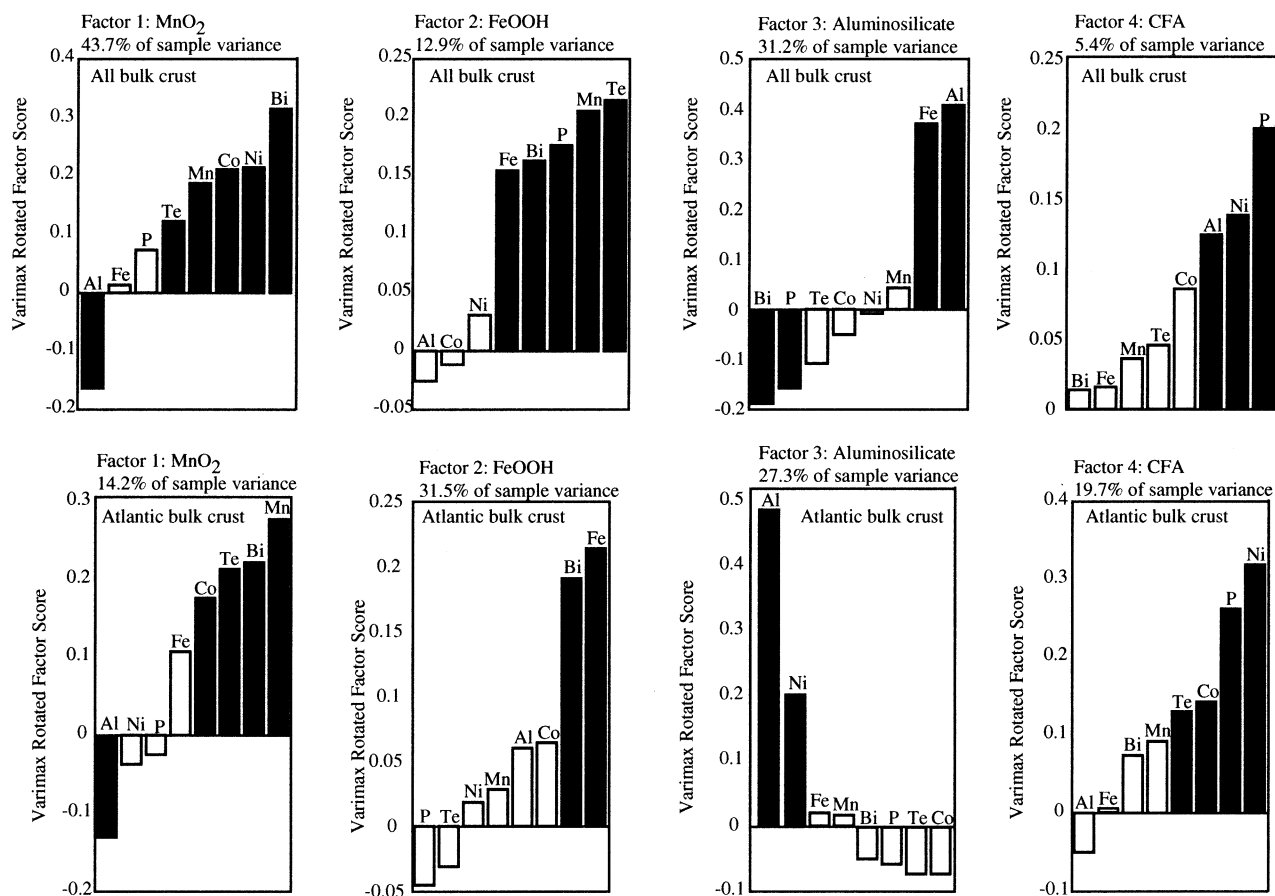


Fig. 3. Graphic display of Q-mode rotated factor scores for selected elements for 2 of the 40 data sets analyzed, all bulk crust data and Atlantic bulk crust data. Elements were selected to represent the FeOOH (Fe), MnO₂ (Mn), CFA (P), and aluminosilicate-detrital minerals (Al) phases in addition to Te and several other trace elements. Solid bars are for elements that are statistically significant members of the factor, and open bars are for elements that fall within the statistical noise.

ocean-water concentrations (Fig. 4). The enrichments of this group range from 600 million for Te to 3 billion for Pb. Although the enrichment factor of Te in Fe-Mn crusts relative to ocean water is very high, it is not as unique as its enrichment

in Fe-Mn crusts compared with the Earth's crustal abundance. This indicates that the uniqueness of Te enrichment in the form of Fe-Mn crust/Earth's crust ratios is the result of large enrichment factors for both seawater/Earth's crust and Fe-Mn crust/seawater, which are multiplicative.

Although the Te contents of individual hydrogenetic Fe-Mn crust samples vary by a factor of nearly 100, the mean values from various regions of the global ocean vary only by a factor of ~7. That variation of mean bulk-crust compositions is explained in part as a dilution of hydrogenetic Te-containing phases by detrital (eolian, hemipelagic, local sources) and hydrothermal inputs. Tellurium is a hydrogenetic component in crusts, along with Mn, Co, and much of the Fe, as indicated by its highest abundances in places away from sources of diluents. The most pure hydrogenetic end member is west-central Pacific (Fig. 2) crusts, the region most removed from terrigenous and hydrothermal inputs. Normalization of mean bulk crust compositions from other regions to that of central Pacific crusts shows that dilution by hydrothermal and detrital sources accounts for only 4 to 25% of the differences in the means. The remainder of the differences is the result of different rates of accretion of the hydrogenetic phases.

Tellurium contents in Fe-Mn crusts are strongly dependent

Table 4. Percentages of Mn, Fe, and Te in four phases from sequential leaches of three Fe-Mn crusts and two hydrothermal Mn samples.

Element	Pacific crust	Pacific crust with CFA	Atlantic crust	Hydrothermal	Hydrothermal
Mn					
Loosely bound	<0.05	<0.05	<0.07	0.0	0.0
Mn phase	98	98.8	99	99.5	99.6
Fe phase	2	1	1	0.5	0.4
Residual	<0.05	0.2	<0.07	0.0	0.0
Fe					
Loosely bound	<0.07	<0.2	<0.2	1	0.1
Mn phase	10.5	23	34	2	1
Fe phase	89	73	59	55	34
Residual	0.5	4	7	42	65
Te					
Loosely bound	5	4	4	14	10
Mn phase	8	10	8	51	54
Fe phase	84	77	84	33	34
Residual	3	9	4	2	2

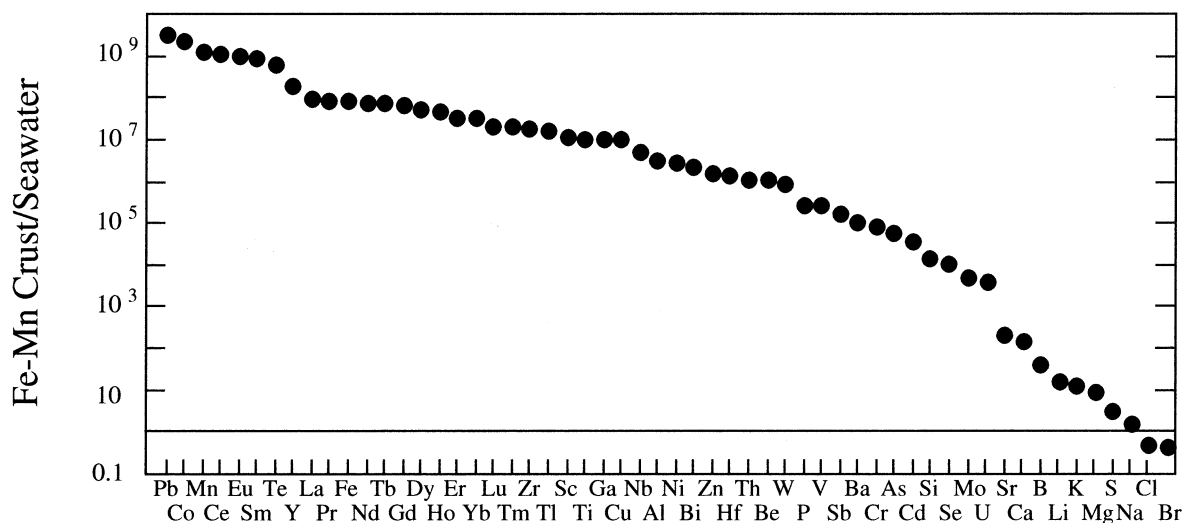


Fig. 4. Enrichment of elements in Fe-Mn crusts relative to their mean abundance in ocean water.

on crust growth rates (Fig. 5). Because most hydrogenetic Fe-Mn crusts accrete at rates between about 1 and 6 mm/Ma (i.e., a factor of 6), the Te contents in those crusts also vary by a factor of ~ 6 as indicated in Figure 5. Growth rates higher than ~ 10 mm/Ma would suggest a hydrothermal or diagenetic contribution to a crust (Hein et al., 2000). Even though the Te concentration varies inversely with growth rate, the flux of Te ($\mu\text{g cm}^{-2} \text{ ka}^{-1}$) to crusts does not vary uniformly with growth rate (Fig. 5). These two characteristics were also found for Co in crusts (Halbach et al., 1983). The flux of Co to crusts is nearly constant in the open ocean (Halbach et al., 1983; Frank et al., 1999) and consequently Co content can be used as a chronometer to determine the growth rates and ages of crusts. Our data are not precise enough to determine whether the flux of Te to crusts is constant, which would require data on Te contents and growth rates for the outermost (recent) growth layer of a group of crusts. The fluxes calculated here are based on data for thick crusts layers and vary by a factor of 10 based on 11 samples, or a factor of 5 if an outlier sample is removed. We speculate that more precise data will show that, like Co, the flux of Te to open-ocean crusts may be nearly constant even though quite small variations in Te flux can be attributed to a relative increased supply rate (relative to growth rate) from the oxygen-minimum zone.

5.2. Incorporation of Te in Fe-Mn Crusts

Sequential leaching clearly shows that most of the Te in Fe-Mn crusts is associated with the FeOOH (Table 4). This association is consistent with the model of Koschinsky and Hein (2003) that relates the phase association of 40 elements in crusts with their respective speciations in ocean water and charge balance. In that model, positively charged species generally adsorb on strongly negatively charged MnO_2 surfaces, whereas neutral and negatively charged species generally bind on slightly positively charged FeOOH surfaces. For the hydrothermal Mn samples (Table 4), about half of the total Te is leached with the Mn oxide (Table 4) and only $\sim 34\%$ with the FeOOH. This difference between hydrothermal deposits and

Fe-Mn crusts reflects the different chemical environments in which they precipitated, the low total Fe concentrations in the hydrothermal deposits, and the predominantly todorokite mineralogy of hydrothermal samples.

Tellurium has a scavenging-type distribution caused by input at the ocean surface, predominantly Te(VI) (Lee and Edmond, 1985), and strong scavenging at depth by particulate matter. Interestingly, the thermodynamically stable Te(IV) is less abundant than Te(VI) in ocean water and Te profiles in part resemble those of Se and Po in ocean water and structurally tellurate should behave like Sn or Po (Lee and Edmond, 1985). A reflection of this similar ocean-water chemistry is the common positive correlation of Te and Sn concentrations for Fe-Mn crusts. The predominance of Te(VI) over Te(IV) in ocean water varies by a factor of 2 to 3.5 (Lee and Edmond, 1985), which is large with respect to the thermodynamic stability of Te(IV) over Te(VI).

The speciation of Te in ocean water is not completely understood, but likely occurs as HTeO_3^- and H_5TeO_6^- , with Te contents ranging from ~ 0.4 to 1.9 pM, in typical oxic ocean water (Andreae, 1984; Lee and Edmond, 1985; Li, 1991; Byrne, 2002; this article). In the first article on Te in ocean water, Te(IV) was reported as the main redox species (Andreae, 1984). Bruland (1983) listed TeO_3^{2-} and HTeO_3^- as the most likely dominant species. Lee and Edmond (1985) found predominantly Te(VI) in water column profiles in the Angola Basin and Panama Basin and stated that it is present as Te(OH)_6^0 rather than as an oxyanion. Li (1991) reported the speciation of each redox form, TeO(OH)_5^- , Te(OH)_6^0 , and TeO(OH)_3^- . The most recent evaluation of the speciation of Te in ocean water indicated that the dominant Te(VI) and Te(IV) species are TeO(OH)_5^- and TeO(OH)_3^- , respectively (Byrne, 2002). None of these possible Te species will affect the phase association in Fe-Mn crusts because both neutral and negatively charged hydroxide complexes and oxyanions bind preferentially on FeOOH surfaces, which includes all the Te(IV) and Te(VI) species reported.

In a recent compilation of thermodynamic data for aqueous

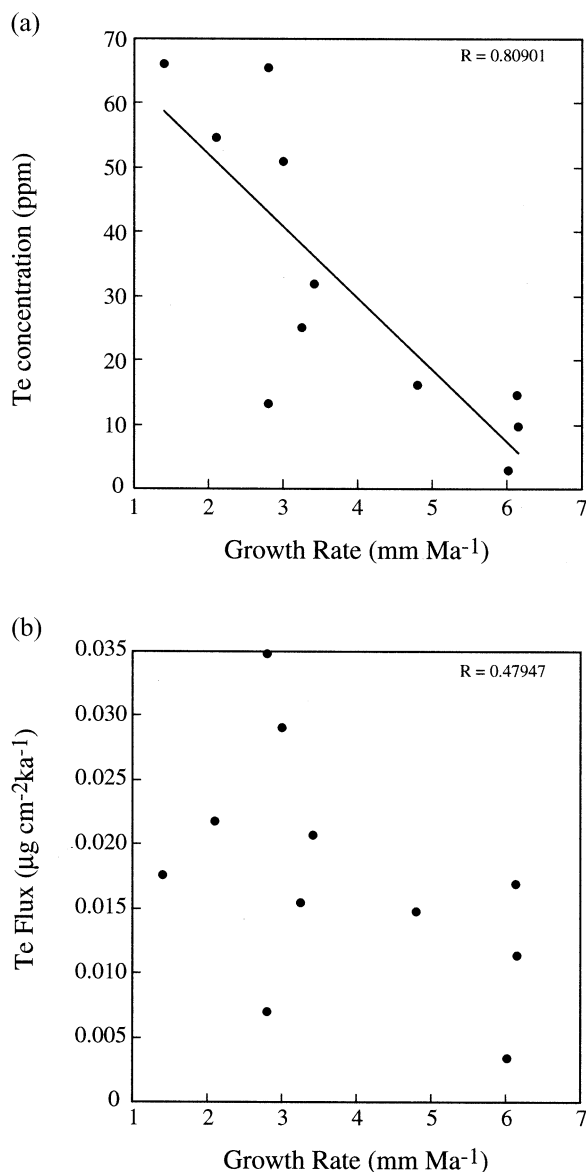
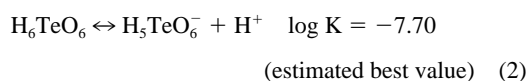


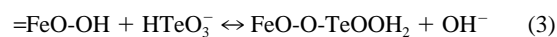
Fig. 5. (a) Te concentration vs. growth rate of Fe-Mn crusts show a statistically significant correlation. (b) Te flux does not vary uniformly with crust growth rate.

Te species (McPhail, 1995), the following equilibrium constants are given for tellurite and tellurate species:



This means that at a ocean water pH of 8, the predominant species are HTeO_3^- and H_5TeO_6^- , in agreement with recent calculations made by Byrne (2002). However, at pH values below 7.7, which may occur in microenvironments, under hydrothermal conditions, or in some Pacific deep waters, H_6TeO_6 would predominate. Sorption of the anionic Te species on the FeOOH surface can be written as a ligand exchange

reaction in which hydroxyl surface groups are replaced by the sorbing ion (after Dzombak and Morel, 1990):



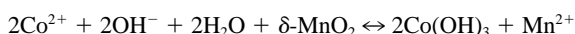
We propose a model in which Te(IV) is preferentially sorbed on FeOOH and is subsequently oxidized to Te(VI). The fact that the various references cited above reported both Te(IV) and Te(VI) as being the dominant or even exclusive redox species in ocean water, the most conclusive work shows that Te(VI) is the dominant ocean-water species (Lee and Edmond, 1985). This contrasts with Te(IV) being the most thermodynamically stable form at low temperature and high oxygen activity (McPhail, 1995). The scavenging-type distribution and strong particle reactivity indicate that a mechanism favoring scavenging of Te(IV) over Te(VI) may control the abundance of Te species in ocean water. This preferential scavenging does not exclude sorption of Te(VI) on FeOOH, but the preferential scavenging of Te(IV) does provide a mechanism that explains the discrepancy between thermodynamic stability and Te species distribution. In our model, oxidative enrichment of Te from the preferential sorption of Te(IV) on FeOOH explains this species distribution (see below) and the extreme enrichments of Te in crusts. Extreme enrichments of Co and Ce in crusts over ocean-water concentrations have been attributed to a surface oxidation process: $\text{Co}^{2+}(\text{aq}) \rightarrow \text{Co}^{3+}(\text{s})$ (Hem, 1978; Murray and Dillard, 1979) and $\text{Ce}^{3+}(\text{aq}) \rightarrow \text{Ce}^{4+}(\text{s})$ (Goldberg et al., 1963; Takahashi et al., 2000). For both elements, an enrichment and oxidation reaction on the Mn-oxide surface involving the oxidation of the dissolved cation by Mn(IV) O_2 is assumed. A surface redox transformation on Mn oxide was also observed for Tl ($\text{Tl}^+ \rightarrow \text{Tl}^{3+}$; Gadde and Laitinen, 1974; Bidoglio et al., 1993) and is assumed to be responsible for the high concentrations of Tl in crusts (factor of 10^7 ; Fig. 4; Koschinsky and Hein, 2003).

Because Te is similarly enriched in crusts (up to nearly 9 orders of magnitude; Fig. 4), we propose that a surface-oxidation process is likely responsible for this enrichment as well. However, this conclusion faces the same problem encountered by Halbach et al. (1989) who suggested mechanisms to explain high concentrations of Pt in crusts. Both the reduced and oxidized forms of possible Pt and Te species (PtCl_4^{2-} , PtCl_6^{2-} , and the Te species mentioned above) are anionic and would therefore not adsorb on the negatively charged colloidal surface of hydrous MnO_2 . As these anionic species would preferentially bind to the slightly positively charged FeOOH surface, we propose that a surface-oxidation process, as has been verified for Co, Tl, and Ce on MnO_2 , is also likely between redox-sensitive species and FeOOH. Oxidation of Ce(III) to Ce(IV) by FeOOH has been shown in scavenging experiments by Bau (1999), where rapid oxidation rates for Ce were found during formation of FeOOH and slower rates were observed when Ce interacted with preformed FeOOH. Also, the oxidation of As(III) on both Mn(IV) and Fe(III) oxides in aqueous systems was observed by several authors (e.g., Oscarson et al., 1981; De Vitre et al., 1991). Belzile et al. (2001) found that Sb(III) reacted similarly to As(III) in that antimonite was rapidly (within days) and completely oxidized to Sb(V) after adsorption on natural and synthetic Fe oxyhydroxides and

synthetic Mn oxyhydroxides. Dissolved oxygen alone did not oxidize Sb(III) within the duration of the study, emphasizing the important role of Fe and Mn oxides in controlling redox reactions in aqueous systems. Because the reduced and oxidized forms of Sb, As, Pt, and Te in ocean water are all either neutral or anionic hydroxide complexes and oxyanions, and show similar behavior with respect to incorporation in Fe-Mn crusts (Koschinsky and Hein, 2003), a similar mechanism of oxidation of Te(IV) on FeOOH as described for As and Sb is realistic. In addition, it is known that the member of chemically similar pairs that undergoes an **oxidation reaction** (e.g., Co-Ni, Ce-Sm(Eu), Tl-Cd, Pt-Pd) is always the more highly enriched member in Fe-Mn crusts. The Te-Se pair would be consistent with that relationship (Fig. 4) in that the enrichment of Se in crusts compared with ocean water is orders of magnitude smaller than for Te. The redox speciations of Se and Te in ocean water are very similar, with Te(VI) and Se(VI) being the dominant forms. In addition, the Te(IV)/Te(VI) and Se(IV)/Se(VI) ratios are quite similar (Measures et al., 1980; Lee and Edmond, 1985; Cutter and Cutter, 2001), which is surprising considering that the most thermodynamically stable forms are different, Te(IV) and Se(VI).

Other elements may be highly enriched in Fe-Mn crusts relative to their ocean water concentrations, such as those situated adjacent to Te in Figure 4 (rare earth elements). However, those elements should not be compared with Te in terms of sorption behaviors because their speciations (carbonate species) are different and only elements with similar speciation types should be compared.

Our proposed model for the enrichment of Te in Fe-Mn crusts includes the oxidation of Te(IV) on FeOOH surfaces. The sorption of Te via reaction (3) is followed by the transfer of two electrons from the sorbed Te to two Fe atoms, and the incorporation of the sorbed and oxidized Te(VI) compound into the FeOOH (Fig. 6). Fe(II) is probably reoxidized to Fe(III) by oxygen in ocean water. The thermodynamic properties of the Te species sorbed on FeOOH are probably different from those of the dissolved Te species in ocean water and need to be determined to make a quantitative thermodynamic assessment of this reaction. The presence of an electric field at the interfacial region has been neglected in simple thermodynamic calculations. It was suggested (e.g., Crerar and Barnes, 1974) that the free-energy equivalent to the specific-adsorption potential should be included in the free energy of a reaction at an oxide interface. Murray and Dillard (1979) used this approach to explain how the oxidation of Co^{2+} on the Mn-oxide surface following the reaction



can still proceed even though it is thermodynamically unfavorable under ocean-water conditions. That oxidation process has been verified by X-ray photoelectron spectroscopy (Dillard et al., 1982). We suggest that similar mechanisms adequately explain the oxidative enrichment of Te on the FeOOH surface. We speculate that this is also the mechanism for the enrichment to Pt in Fe-Mn crusts.

Our model can be tested in a number of ways. Determination of the thermodynamic properties of Te species sorbed on FeOOH will create a basis for equilibrium calculations. Exper-

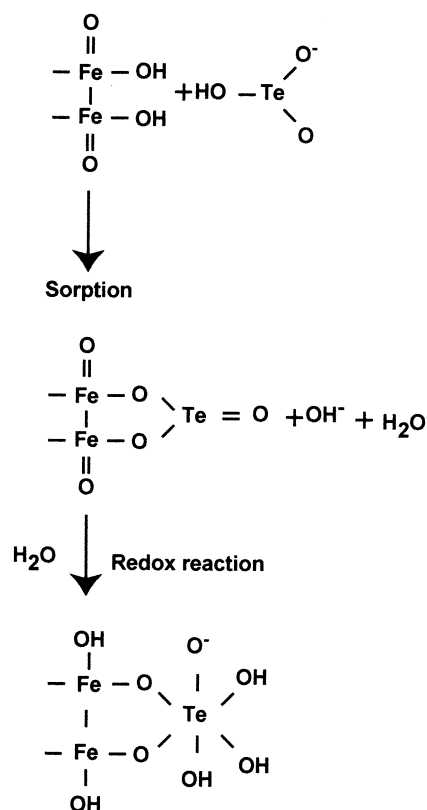


Fig. 6. Schematic representation of the surface reaction involving sorption of tellurite on the FeOOH surface and electron transfer.

iments need to be performed that compare the sorption of Te(IV) and Te(VI) on crusts and Te on pure FeOOH and MnO_2 . Tellurium speciation in crusts can be determined by the chemical techniques of Ferri et al. (1998) and its oxidation state by synchrotron radiation techniques (e.g., X-ray absorption near-edge spectroscopy, extended X-ray absorption fine structure). However, Te does not exist in high enough concentrations in Fe-Mn crusts to derive structural information by synchrotron techniques (A. Foster, personal communication).

5.3. Partial Mass Balance for Tellurium in the Oceans

The mass balance of Te is speculative because the Te fluxes from eolian, anthropogenic, and hydrothermal sources to the oceans are not known. Further, an extensive search of the literature has yielded only one Te determination for river water, the Ming River in China, which has a Te content of 2.8 ng L^{-1} (21.9 pM; Table 1). Samples from seven sites on two rivers in the United Kingdom yielded only concentrations below the detection limit of 50 ng L^{-1} (0.39 nM; Thompson et al., 1981). However, if we take the mean Te content of ocean water to be 0.1 ng L^{-1} (0.8 pM) and that of rivers to be 3 ng L^{-1} (23.5 pM), then the scavenging residence time of Te in the oceans would be $\sim 1000 \text{ yr}$. Considering that the Te profile in ocean water is controlled by scavenging at depth and its very high reactivity (Lee and Edmond, 1985), this residence time would be a possible maximum. If the mean global flux from rivers were lower by an order of magnitude, then the residence time

would be 10,700 yr, an unrealistically large residence time; and if the flux were higher by an order of magnitude, the residence time would be 107 yr, a likely residence time when compared with those of other reactive metals and this is the value used here. From a structural viewpoint, the residence time of Te in deep-ocean water should be very similar to those of ^{210}Po and ^{210}Pb , ~50 to 100 yr, comparable to the our calculated residence of 107 yr. These calculations, and comparisons with other reactive elements, indicate that the global mean Te content of river water should be $\sim 30 \text{ ng L}^{-1}$ (0.24 nM), which is the value we use for mass balance calculations.

The mean Te content of global rivers can also be calculated by comparing Te to a geochemically similar element such as Se. By use of a Se/Te ratio approximately equal to 10 for the Earth's crust (based on 5 ppb Te; Krauskopf, 1979; Govett, 1983) and the mean Se content of rivers, we calculate a global mean Te content for river water of 20 ng L^{-1} (0.16 nM). This value is in reasonably good agreement with the best estimate from residence time considerations.

To determine the amount of Te stored in Fe-Mn crusts, we provide the first calculation of the total mass of Fe-Mn crusts in the global ocean. This calculation is made from an estimate of the amount of hard rock exposed on seamounts, plateaus, ridges, and fracture zones in the global oceans gleaned from the literature, from data collected on 46 cruises dedicated to the study of Fe-Mn crusts, and from 30 other cruise reports. The mean crust thickness for each type of topographic feature and region of the global ocean was derived from our database on globally distributed Fe-Mn crusts, from cruise reports, and data from the literature, which in total provide more than 3000 thickness measurements. These calculations indicate that the area of ocean floor covered by Fe-Mn crust is $6.35 \times 10^{16} \text{ cm}^2$. To calculate tonnage, a 1.3 g/cm^3 dry bulk Fe-Mn crust density was used (Hein et al., 2000). From these data, a conservative estimate of the total dry bulk mass of hydrogenetic Fe-Mn crusts on seamounts, ridges, fracture zones, and plateaus in the global ocean is 2×10^{11} tonnes. The corresponding mass of incorporated Te would be 9 million tonnes, which is 67 times the amount of Te presently dissolved in ocean water and ~7000 to 8500 yr of river supply. For comparison, it has been estimated that there are 0.9×10^{11} to 1.5×10^{12} tonnes of abyssal Fe-Mn nodules in the Pacific (Mero, 1965).

Fe-Mn crusts are a sink for ~20% of the annual input of Te from rivers on the basis of the calculated flux (Fig. 5) for the thinnest crust interval analyzed. However, this estimate could be as low as 2% or as high as 40% allowing for uncertainties in the mean Te content of rivers and flux rates. The calculated flux rates reflect integrated rates for several millions of years of crust growth. Fe-Mn abyssal nodules are a sink for 8 to 80% of the annual river flux of Te. Hydrothermal Mn deposits, which form under an ocean-water-dominant system, are enriched in Te only ~6 to 100 times over its maximum Earth's crustal abundance, but these deposits still act as a significant global sink for Te. The accumulation of trace metals for Fe-Mn crusts begins with the scavenging of those metals by Fe-Mn colloids in the water column (e.g., Koschinsky and Halbach, 1995). Our order-of magnitude calculations indicate that Fe-Mn deposits are the dominant sink for Te in the oceans, and that they, along with Fe-Mn colloids in the water column, may control the

concentration and redox speciation of Te in the global ocean, which is also the case for Ce.

6. SUMMARY AND CONCLUSIONS

Hydrogenetic Fe-Mn crusts are distributed throughout the ocean basins where bare rock is exposed at the ocean floor and they concentrate most elements because of very slow growth rates and extremely large specific surface area. Tellurium is enriched by 5000 to 50,000 times in Fe-Mn crusts relative to its mean content in the Earth's crust. This enrichment is orders of magnitude greater than any other element in Fe-Mn crusts. Tellurium concentrations in open-ocean crusts are greater than those in continental margin crusts and hydrothermal Mn deposits. Sequential leaching shows that the Te is associated predominantly with the FeOOH in Fe-Mn crusts. The enrichment of Te in the amorphous FeOOH can be explained by sorption of both aqueous tellurite and tellurate species, but with tellurite being favored. The extreme enrichment of Te in Fe-Mn crusts compared with species that are geochemically similar, such as Se, indicates the existence of a special enrichment process. We propose that this process is the oxidation of Te^{4+} to Te^{6+} on the FeOOH surface. Because reactions between tellurite and tellurate species are very slow and equilibrium has not been demonstrated (McPhail, 1995), a surface oxidation enrichment that preferentially acquires Te(IV) from ocean water can explain the dominance of the thermodynamically less stable Te(VI) over Te(IV) in ocean water.

Mass-balance calculations indicate that ocean-floor Fe-Mn deposits comprise the ultimate major sink for Te in the oceans. Together with scavenging by Fe-Mn colloids in the water column, this sink controls the concentration and redox speciation of Te in the global ocean.

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